

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE

30 October 1996

3. REPORT TYPE AND DATES COVERED

Technical

4. TITLE AND SUBTITLE

FACILE PREPARATION OF NANOCRYSTALLINE
GALLIUM ANTIMONIDE

5. FUNDING NUMBERS

•N00014-95-1-0194
R&T Project 3135008---16
•N00014-93-1-0860
R&T Project 4135008---13
•Dr. Harold E. Guard

6. AUTHOR(S)

R. A. Baldwin, E. E. Foos, and R. L. Wells

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Department of Chemistry
Duke University
Durham, NC 27708-0346

8. PERFORMING ORGANIZATION
REPORT NUMBER

Technical Report
No. DU/DC/TR-64//AASERT-06

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
300 North Quincy Street
Arlington, VA 22217-5000

10. SPONSORING / MONITORING
AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Accepted for publication in *Materials Research Bulletin*

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for Public Release
Distribution Unlimited

12b. DISTRIBUTION CODE

19961113 031

13. ABSTRACT (Maximum 200 words)

The 1:1 reaction of GaCl_3 with $\text{Sb}(\text{SiMe}_3)_3$ in pentane solution affords an intermediate material which, upon thermolysis, yields nanocrystalline GaSb with an approximate average particle size of 12 nm. The product was characterized through powder X-ray diffraction, elemental analysis, and HRTEM.

DTIC QUALITY INSPECTED 2

14. SUBJECT TERMS

gallium antimonide, nanocrystalline,

15. NUMBER OF PAGES
8

16. PRICE CODE

17. SECURITY CLASSIFICATION
OF REPORT

Unclassified

18. SECURITY CLASSIFICATION
OF THIS PAGE

Unclassified

19. SECURITY CLASSIFICATION
OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT
Unlimited

OFFICE OF NAVAL RESEARCH

Grant N00014-95-1-0194
R&T Project 3135008---16

and

Grant N00014-93-1-0860
R&T Project 4135008---13

Dr. Harold E. Guard

Technical Report No. DU/DC/TR-64//AASERT-06

FACILE PREPARATION OF NANOCRYSTALLINE GALLIUM ANTIMONIDE

Ryan A. Baldwin, Edward E. Foos, and Richard L. Wells

Accepted for publication in *Materials Research Bulletin*

Duke University
Department of Chemistry,
P. M. Gross Chemical Laboratory
Box 90346
Durham, NC 27708-0346

30 October 1996

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited.

FACILE PREPARATION OF NANOCRYSTALLINE GALLIUM ANTIMONIDE

RYAN A. BALDWIN, EDWARD E. FOOS, and RICHARD L. WELLS

Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University

Durham, North Carolina 27708, U.S.A.

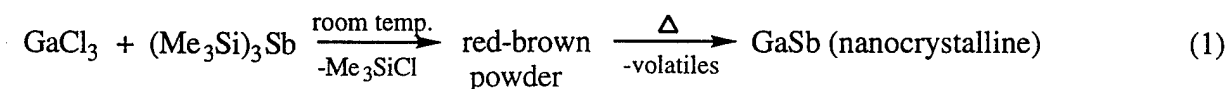
Abstract: The 1:1 reaction of GaCl_3 with $\text{Sb}(\text{SiMe}_3)_3$ in pentane solution affords an intermediate material which, upon thermolysis, yields nanocrystalline GaSb with an approximate average particle size of 12 nm. The product was characterized through powder X-ray diffraction, elemental analysis, and HRTEM.

Keywords: A. Nanostructures, A. Semiconductors, B. Chemical Synthesis, C. Electron Microscopy, C. X-Ray Diffraction.

Introduction

Nanocrystalline 13-15 semiconductors have attracted much attention recently due to their interesting electronic and optical properties (1) and, as a result, synthetic pathways to these materials have been investigated extensively over the past few years (2). In 1989, the first use of dehalosilylation reactions to prepare the 13-15 compound semiconductors ME ($\text{M} = \text{Ga}$ (3a), In (3a), and Al (3b), $\text{E} = \text{As}$; $\text{M} = \text{In}$ (3c, d), $\text{E} = \text{P}$) was reported. Since that time, researchers in our laboratory (4) and in others (5) have utilized this methodology to prepare 13-15 materials of nanoscale dimensions. While the use of dehalosilylation to prepare nanocrystalline Group 13-phosphides (4, 5b, d) and -arsenides (5a, c) is well documented, the preparation of Group 13-antimonides by this method has been studied less extensively (*vide infra*). Gallium antimonide-based compound semiconductors, for example, have recently been of interest for their potential in electronic applications (6).

A literature review finds that numerous researchers have prepared gallium antimonide (GaSb) in the solid and vapor phases (6, 7), however, solution phase preparations are limited (2b). In an attempt to remedy this situation, we recently reported the production of GaSb by a solution-phase silyl halide elimination method and examined the purity, crystallinity, and particle size of the resultant product in a detailed manner (8). The utility of this method has also been demonstrated recently by Schulz *et al.* (9). Herein, we detail our results for the 1:1 mole reaction of gallium(III) chloride with tris(trimethylsilyl)stibine in pentane solution to afford an intermediate material which, upon annealing, afforded nanocrystalline GaSb (eq. 1).



Experimental

All manipulations of air and moisture sensitive materials were performed in a Vacuum Atmospheres HE-493 Dri-Lab containing an argon atmosphere or by general Schlenk techniques. Pentane was distilled from Sodium/Potassium alloy under dry dinitrogen. GaCl₃ was purchased from Strem Chemicals and was used as received without further purification. GaSb was purchased from Alfa AESAR and used as received. Tris(trimethylsilyl)stibine, (Me₃Si)₃Sb, was prepared according to literature methods (10) with slight modifications. Elemental analysis was performed by E+R Microanalytical Laboratory, Inc., Corona, NY. X-ray powder diffraction (XRD) data were obtained on a Philips XRG 3000 diffractometer using Cu Kα radiation (λ = 1.5418 Å; graphite monochromator). Transmission electron microscopy (TEM) data were collected on a TOPCON EM002B instrument utilizing a 200 kV accelerating voltage at the North Carolina State University Analytical Instrumentation Facility.

A 250 mL round-bottomed flask equipped with a Teflon valve and a stir bar was charged with Sb(SiMe₃)₃ (0.682 g; 2.00 mmol) dissolved in 30 mL of pentane. To this clear, slightly yellow solution, GaCl₃ (0.352 g; 2.00 mmol) dissolved in 25 mL of pentane was added *via* pipet. An immediate orange-red color developed with the formation of a dark precipitate. This mixture

was allowed to stir for 12 h at room temperature. The volatiles were removed *in vacuo* to yield a red-brown powder (0.439 g) of empirical formula $C_2H_6Ga_2SbCl$ (based upon C, H, Ga, Sb, Cl analyses) which was isolated as an intermediate material. The volatiles were then hydrolyzed with deionized water and titrated with NaOH (0.0997 M, 17.10 mL, corresponding to the elimination of 1.70 mmol (56.7%) of Me_3SiCl).

The gallium-antimony containing intermediate was thermally decomposed as follows: The red-brown powder was loaded into a sublimator, heated under vacuum at 75 °C for 15 min., and then ramped by 30 °C increments from 75 to 285 °C, 20 °C increments from 285 to 325 °C, and 25 °C increments from 325 to 400 °C. Sustained heating of the sample at 400 °C for 24 h afforded a black powder containing GaSb (0.227 g; 59% yield based on Ga) with only a trace of by-product residue detected on the sublimator coldfinger. Hydrolysis and titration of the decomposition volatiles yielded only 0.1 mmol (3.3%) of detectable Me_3SiCl . Anal. Calcd(found) for GaSb: Sample 1, Ga, 36.41(23.53); Sb, 63.59(59.14); C, 0.00(1.80); H, 0.00(0.37); Cl, 0.00(<0.30); Ga:Sb ratio 1.0:1.4; Sample 2, Ga, 36.41(25.63); Sb, 63.59(49.82); C, 0.00(1.06); H, 0.00(0.28); Cl, 0.00(2.78); Si, 0.00(1.64); Ga:Sb ratio 1.0:1.1.

Results and Discussion

A powder X-ray diffraction (XRD) pattern of the red-brown intermediate material showed it to be amorphous in nature. Annealing this powder at 400 °C for 24 h afforded a black powder containing GaSb, initially confirmed by elemental analysis (EA). From the EA results, *vide infra*, the Ga:Sb ratio was calculated as 1:1.4, indicating that there was excess antimony present in the sample. Thus, the sample composition was calculated as 65% GaSb (Ga and Sb constitute 83% of the sample weight) with minimal contamination from carbon and essentially none from hydrogen or chlorine. Since the initial sample was not analyzed for silicon content, we could not conclude with complete certainty that the remaining impurity was silicon. To resolve this question, we submitted a second sample of the annealed material for full elemental analysis (C, H, Cl, Si, Ga, Sb). For the second sample, the Ga:Sb ratio was calculated as 1:1.1,

indicating that excess antimony was still present in the powder. The GaSb composition of this sample was calculated as 70% (Ga and Sb constitute 75% of the sample weight) with minimal contamination from carbon, hydrogen, chlorine, and silicon. To date, we are unable to unambiguously account for the remaining sample percent composition and studies are ongoing to address this issue.

The XRD pattern of the black powder obtained from the reaction (eq. 1) is shown in Figure 1. Comparison of this plot with an XRD pattern of a bona fide sample of 99% pure GaSb confirms the presence of GaSb in the powder. The labeled peaks in Fig. 1 correspond to the (111), (220), and (311) reflections of cubic GaSb, as reported by JCPDS (11). In agreement with the EA results, there are peaks in the XRD pattern which indicate the presence of excess antimony, most notably the peak at 40° 2θ angle, which matches the (104) reflection of hexagonal Sb. The large peak at 29° 2θ matches both the (200) reflection of cubic GaSb and the (012) reflection of hexagonal Sb, however, it is unclear which species is responsible for its presence. Due to the relative intensity of this peak, it is conceivable that it has contributions from both the (200) GaSb and (012) Sb lattice planes; however, no attempt was made to resolve these peaks. Using the XRD data, an approximate average particle size of 12 nm was calculated for the sample by the Scherrer equation (12).

Fig. 1. XRD pattern of annealed GaSb nanocrystals. A 12 nm approximate average particle size was calculated for the specimen from the XRD data. The y-axis shows relative intensity.

Figure 2 shows a section of the high-resolution transmission electron micrograph (HRTEM) obtained on the GaSb containing sample. The majority of the lattice fringes observed correspond to the (111) reflection plane of cubic GaSb, however, lattice fringes corresponding to the (220) reflection plane are also visible. The d-spacings corresponding to these reflections are 3.5 and 2.2 Å, respectively, and by counting the number of planes observed for a particular crystallite, its size may be approximated. The range of crystallite sizes obtained from this

procedure is in good agreement with the average size calculated from the XRD data. As further evidence of the sample identity, an electron diffraction ring pattern of the sample was indexed to that of cubic GaSb (11). It is interesting to note that a small number of particles are present in the TEM images (though none are seen in Figure 2) which match the 3.1 Å d-spacing of the (012) reflection of hexagonal Sb. This is not surprising, though, considering that the EA and XRD results have established the presence of excess antimony in the sample.

Fig. 2. Transmission electron micrograph (TEM) of the GaSb quantum particles. The marker represents the scale. Lattice planes of several small crystallites are visible.

The preliminary EA, XRD, and HRTEM data given above suggest that nanocrystalline GaSb has been formed by the silyl elimination route. This result is significant in that it represents, to the best of our knowledge, the first preparation of GaSb under these conditions. Future studies in this area will focus on optimizing the reaction and decomposition conditions to produce higher-quality GaSb, as well as forming other Group 13-antimonides.

Acknowledgments: We would like to thank Drs. Jerzy F. Janik and Shreyas S. Kher for their valuable assistance and suggestions. R. A. B. wishes to thank the AT&T Bell Laboratories (Lucent Technologies) CRFP Program for a graduate fellowship. This work was supported by the Office of Naval Research (ONR) through both a regular research grant and the ONR-AASERT program.

References

- [1] See for example the following and references therein: (a) R. W. Siegel, *Physics Today* **46**(10), 64 (1993). (b) A. P. Alivisatos, *Science* **271**, 933 (1996). (c) *Nanotechnology: Molecularly Designed Materials*; G.-M. Chow, K. E. Gonsalves Eds.; ACS Books, (1996).
- [2] See for example the following: (a) R. L. Wells, R. B. Hallock, A. T. McPhail, C. G. Pitt, J. D. Johansen, *Chem. Mater.* **3**, 381 (1991). (b) S. S. Kher, R. L. Wells, *Mat. Res. Soc. Symp. Proc.* **351**, 293 (1994). (c) S. S. Kher, R. L. Wells, *Chem. Mater.* **6**, 2056 (1994). (d) L. I. Halaoui, S. S. Kher, M. S. Lube, S. R. Aubuchon, C. R. S. Hagan, R. L. Wells, and L. A. Coury, Jr. in *Nanotechnology: Molecularly Designed Materials*; G.-M. Chow, K. E. Gonsalves, Eds., Chap. 12, ACS Books (1996).
- [3] (a) R. L. Wells, C. G. Pitt, A. T. McPhail, A. P. Purdy, S. Shafieezad, R. B. Hallock, *Chem. Mater.* **1**, 4 (1989). (b) R. L. Wells, C. G. Pitt, A. T. McPhail, A. P. Purdy, S. Shafieezad, R. B. Hallock, *Mat. Res. Soc. Symp. Proc.* **131**, 45 (1989). (c) M. D. Healy, P. E. Laibinis, P. D. Stupik, A. R. Barron, *Mat. Res. Soc. Symp. Proc.* **131**, 83 (1989). (d) M. D. Healy, P. E. Laibinis, P. D. Stupik, A. R. Barron, *J. Chem. Soc., Chem. Commun.* 359 (1989).
- [4] (a) S. R. Aubuchon, A. T. McPhail, R. L. Wells, J. A. Giambra, J. R. Bowser, *Chem. Mater.* **6**, 82 (1994). (b) R. L. Wells, S. R. Aubuchon, S. S. Kher, M. S. Lube, *Chem. Mater.* **7**, 793 (1995).
- [5] (a) M. A. Olshavsky, A. N. Goldstein, A. P. Alivisatos, *J. Am. Chem. Soc.* **112**, 9438 (1990). (b) A. P. Alivisatos, A. N. Goldstein *U. S. Patent No.* 5,262,357 (November 16, 1993). (c) L. Butler, G. Redmond, D. Fitzmaurice, *J. Phys. Chem.* **97**, 10750 (1993). (d) O. I. Micic, C. J. Curtis, K. M. Jones, J. R. Sprague, A. R. Nozik, *J. Phys. Chem.* **98**, 4966 (1994).
- [6] See the following and references therein: F. S. Juang, Y. K. Su, N. Y. Li, K. J. Gan, *J. Appl. Phys.* **68**, 6383 (1990).
- [7] (a) R. E. Treece, E. G. Gillan, R. M. Jacubinas, J. B. Wiley, R. B. Kaner, *Mat. Res. Soc. Symp. Proc.* **271**, 169 (1992). (b) R. E. Treece, G. S. Macala, L. Rao, D. Franke, H. Eckert, R. B. Kaner, *Inorg Chem.* **32**, 2745 (1993).
- [8] R. A. Baldwin, E. E. Foos, R. L. Wells, G. P. A. Yap, A. L. Rheingold, *Abstracts of Papers, 211th American Chemical Society National Meeting*, New Orleans, LA, Abstract INOR 198, March 24-29 (1996).
- [9] S. Schulz, L. Martinez, and J. L. Ross, *Adv. Mater. for Optics and Electronics* **6**, 185 (1996).
- [10] (a) A. Sladek, H. Schmidbaur, *Chem. Ber.* **128**, 565 (1995). (b) E. Amberger, R. W. Salazar, *J. Organomet. Chem.* **8**, 111 (1967).
- [11] Joint Committee on Powder Diffraction Standards (JCPDS), File No. 7-215, GaSb.
- [12] H. P. Klug, L. E. Alexander *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*; 491, John Wiley and Sons: New York, (1962).

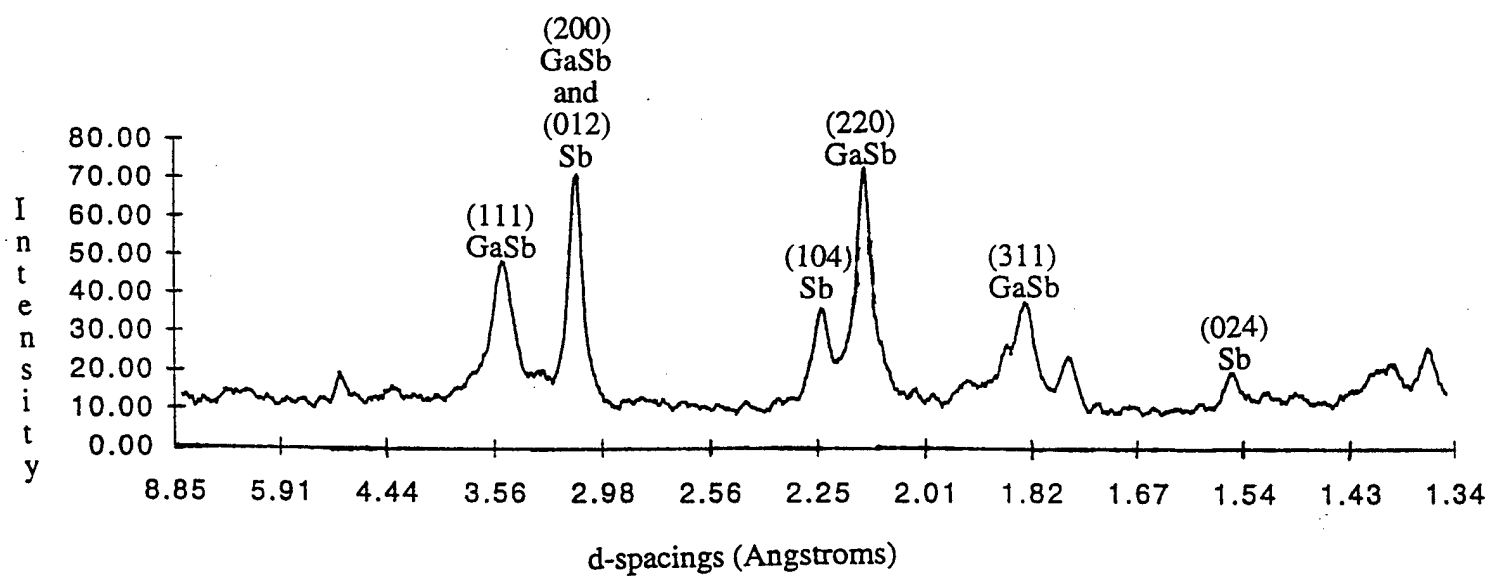


Figure 1.

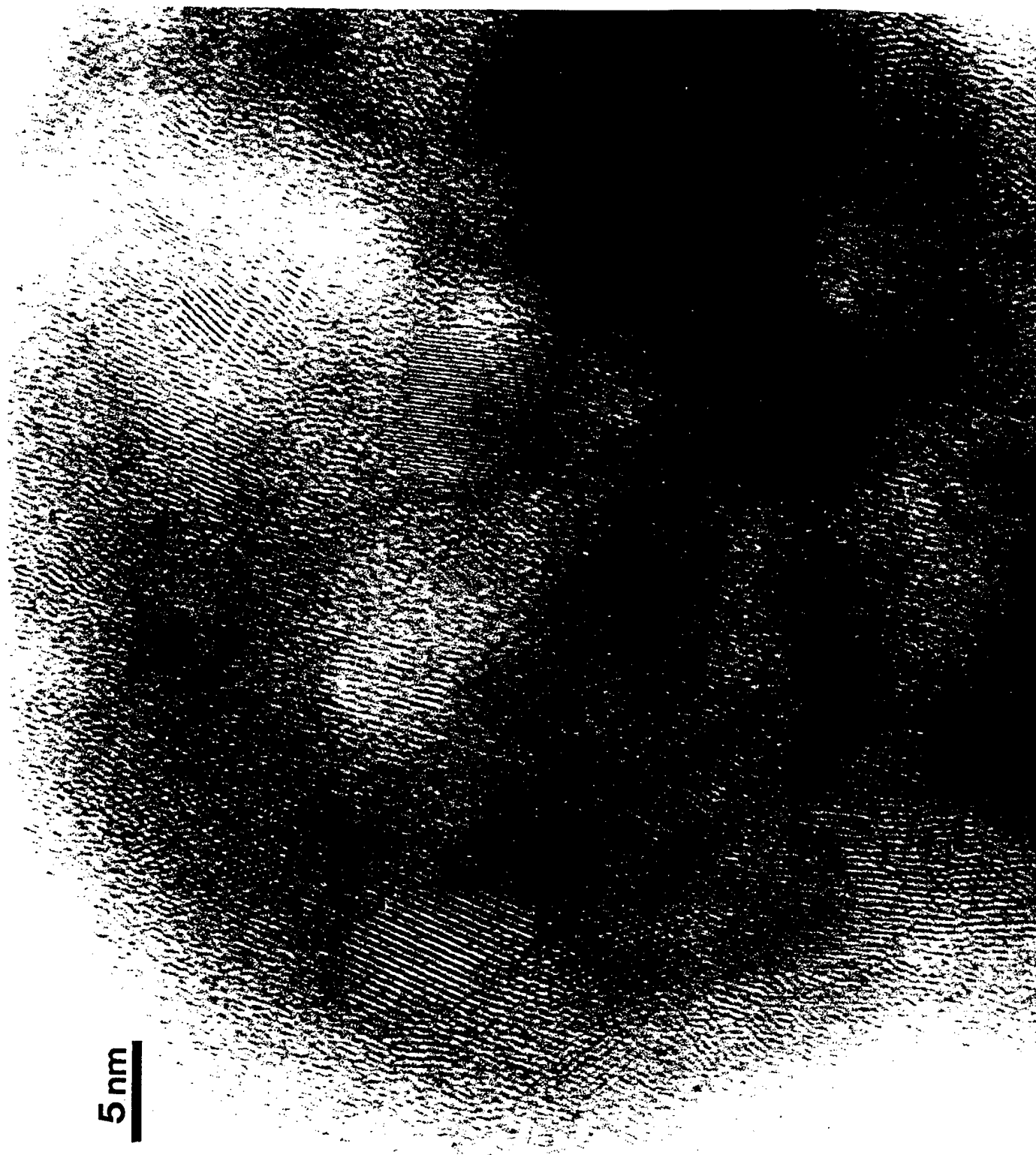


Figure 2.

TECHNICAL REPORTS DISTRIBUTION LIST

ORGANOMETALLIC CHEMISTRY FOR ELECTRONIC & OPTICAL MATERIALS

Dr. Harold E. Guard
Code 1113
Chemistry Division, 331
Office of Naval Research
800 N. Quincy Street
Arlington, Va 22217-5660

Dr. Richard W. Drisko
Naval Facilities & Engineering
Service Center
Code L52
Port Hueneme, CA 93043

Defense Technical Information
Center
Building 5, Cameron Station
Alexandria, VA 22314

Dr. Eugene C. Fischer
Code 2840
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Dr. James S. Murday
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, DC 20375-5320

Dr. Bernard E. Douda
Crane Division
Naval Surface Warfare Center
Crane, IN 47522-5000

Dr. John Fischer, Director
Chemistry Division, C0235
Naval Air Weapons Center
Weapons Division
China Lake, CA 93555-6001

Dr. Peter Seligman
Naval Command, Control and
Ocean Surveillance Center
RDT&E Division
San Diego, CA 93152-5000